



Faculty of Resource Science and Technology

**DETERMINATION OF CADMIUM IN SOILS OF SAMAJAYA
AND BDC, KUCHING**

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Determination of Cadmium in Soils of Samajaya and BDC, Kuching.

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A dissertation submitted in partial fulfilment of the requirement for
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List of Abbreviations

Cd	-	Cadmium
CEC	-	Cation Exchange Capacity
g	-	Gram
GPS		Global Positioning System
HCl	-	Hydrochloric Acid
HNO ₃	-	Nitric Acid
ICP-OES	-	Inductively Coupled Plasma Atomic Emission Spectroscopy
M	-	Molarity
mg/kg	-	Milligram per kilogram
ml	-	Millilitre
mm	-	Millimetre
rpm	-	Revolutions per minute
SOM	-	Soil Organic Matter
SPSS	-	Statistical Packages for the Social Sciences
USEPA	-	United State Environmental Protection Agency
µg/g	-	Microgram per gram

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Determination of Cadmium in Soil of Samajaya and BDC, Kuching.

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Abstract

In recent years, heavy metal contamination in soil has received a lot of attention as it causes significant environmental issues and risks to human health. In this study, the cadmium content in soils of Samajaya and BDC, Kuching was determined using inductive coupled plasma-optical emission spectroscopy (ICP-OES). Soil samples were collected from industrial area, Samajaya Free Industrial Zone and residential area, BDC. The results obtained shows that the mean concentration of 0.160 mg/kg is lower than European Union Standard for cadmium in soils (3.00 mg/kg). Also, the mean concentration of cadmium in soils of industrial area (0.19 mg/kg) is higher than residential area (0.13 mg/kg). By referring to the geoaccumulation index (I_{geo}), soils from 4 sampling points were revealed under the category of "heavily contaminated" and another 4 sampling points were categorized as "uncontaminated". Furthermore, correlation analysis was done between soil pH and soil organic matter with cadmium concentration in soil and results obtained show no significant correlation between both the physical properties with cadmium concentration in soils.

Keywords: Cadmium in soils, urban area, industrial area, residential area

Abstrak

Pada tahun belakangan ini, pencemaran logam dalam tanah telah mendapat banyak perhatian kerana ia telah menyebabkan isu-isu pencemaran dan risiko kepada kesihatan manusia. Dalam kajian ini, kandungan kadmium dalam tanah Samajaya and BDC, Kuching telah dianalisis dengan menggunakan induktif ditambah plasma-optik spektroskopi emisi (ICP-OES). Sampel tanah telah dikumpulkan dari kawasan perindustrian, Samajaya Zon Perindustrian Bebas dan kawasan perumahan, BDC. Hasilannya menunjukkan bahawa purata kepekatan kadmium iaitu 0.160 mg/kg adalah lebih rendah daripada European Union Standard untuk kadmium dalam tanah (3.00 mg/kg). Selain itu, purata kepekatan kadmium dalam tanah kawasan industri (0.19 mg/kg) adalah lebih tinggi daripada tanah kawasan perumahan (0.13 mg/kg). Merujuk kepada indeks indek geoakumulasi (I_{geo}), tanah daripada 4 kawasan persampelan adalah dalam kategori "tercemar parah" dan 4 kawasan persampelan adalah di bawah kategori "tidak tercemar". Tambahan pula, analisis korelasi telah dibuat antara pH tanah dan bahan organik tanah dengan kepekatan kadmium dalam tanah dan keputusan yang diperolehi menunjukkan tiada hubungan signifikan antara kedua-dua ciri-ciri fizikal dengan kepekatan kadmium dalam tanah.

Kata Kunci : Kadmium dalam tanah, Bandar, kawasan industri, kawasan perumahan

1.0 Introduction

Urban area possesses many sources of heavy metals because of the high population density and intense anthropogenic activities. Chemical industry, domestic waste and transportation may continuously adding heavy metals into urban soils. The heavy metals will remain present for a long period although the pollution sources have been removed (Chen, Xia, Zhao, & Zhang, 2010). As a consequence, as mentioned by Ramakrishnaiah and Somashekar (2002) soil quality deteriorates and it becomes an issue to concern at most of the major cities.

Naturally, the presence of cadmium is in companion with zinc, copper and lead in ore (Järup, 2003). Studies showed that cadmium in soils may be originated from dense traffic, domestic disposal or building construction, vehicles tires or fuses, parent material in soil, industry plants and fertilizers (Chen et al., 2010; Deska, Sombik, Marciniuk-Kluska, & Rymuza, 2011; Praszyński, & Wieczorek, 1999; Massadeh, Tahat, Jaradat, & Al-Momani, 2007; Nabulo, Oryem-Origa, & Diamond, 2006). It is often used as stabilizer in polyvinyl chloride (PVC) products, colour pigment, alloys and re-chargeable nickel-cadmium batteries, also as an antioxidant. These products are hardly to be recycled and usually discarded as domestic waste, hence polluting the environment (Järup, 2003).

Cadmium is grouped under heavy metals of anthropogenic origin and it is extremely hazardous for human (Deska et al., 2010). It can be accumulated in human body through ingestion, direct inhalation, and dermal contact absorption (Elbagermi, Edwards, & Alajtal, 2013). Due to its relatively long biological half-life and it is accumulated particularly in liver and kidney for 20 to 30 years. Serious conditions such as osteoporosis, anemia, eosinophilia, emphysema, and renal tubular damage may be arisen as a result of exposure to cadmium. Long-term cadmium exposure may cause an individual to suffer from bone fractures, serious pain, proteinuria, and severe osteomalacia, which are the symptoms of

Itai Itai disease (Akan, Audu, Mohammed.& Ogugbuaja, 2013). Furthermore, cadmium is reported as a human carcinogen by Dertmar, Christoph, and Malviya (1994). Hence, analysis of cadmium is important in urban environmental assessment due to their potential hazard (Sutherland, 2000).

Kuching, as the capital of Sarawak, has been developing in a fast rate and this causes a lot of anthropogenic pressure on it. Contamination of cadmium in soils from both industrial and residential areas will be studied in this research since there has been no study conducted to determine the cadmium content in soil of Kuching City before. The aim of this study was to determine the cadmium concentration of soils in Kuching City in order to compare with European Union Standard of 3.0 mg/kg as mentioned by Hong, Law, and Selaman (2014). Also, to assesses the level of cadmium in industrial area and residential area.

2.0 Literature Review

2.1 Heavy Metals

Rapid urbanization and industrialization in recent years created large number of sources of heavy metals in metropolises. Domestic waste, chemical industry and transportation has been continuously adding heavy metals to the soils and they will stay for many years even after the pollution sources have been removed (Chen et al., 2010). The presence of heavy metal act as the indicator of human exposure to heavy metals as it is important pollutants in urban area (Li, Holm, Marcussen,& Hansen, 2013). Soil pollution and prominent heavy metal uptake by crop may happen as a result of accumulation of heavy metals in agricultural land and finally degrade the quality and safety of food. These heavy metals will eventually get into human body as the food chain has already contaminated by these hazardous pollutants (Naser, Sultana, Gomes,& Noor, 2012).

2.2 Heavy Metals in Urban Areas

In recent years, many studies have been done in order to study the concentration and distribution of heavy metals in soil of urban areas. The concentration of arsenic, cadmium, chromium, copper, nickel, lead and zinc in roadside soil of Beijing were being studied in detail by Chen et al. (2010) in order to analyze how urban traffic would affect the concentration of these heavy metals in soil. Besides, a study was conducted in Kampala City, Uganda to assess the relationship between traffic density and concentration of lead, zinc and cadmium in roadside soils (Nabulo et al., 2006). In addition to that, an overview was done in 31 metropolises in China to deliver a latest assessment of arsenic, cadmium, chromium, copper, mercury, nickel, lead, antimony, selenium, and zinc contamination in soils (Cheng et al., 2013). Also, a study was conducted in Kangar, Perlis in order to assess

the concentration of five heavy metals copper, cadmium, nickel, lead and zinc in soil from six selected sites with different human activities (Najib, Mohammed, Ismail, & Ahmad, 2012).

2.3 Background Information of Cadmium

A study was done in Kosovo to determine the distribution of cadmium in urban soil. The result shows that the mean concentration of cadmium is 3.25 mg/kg with the highest concentration of 46.8 mg/kg and lowest concentration of 0.18 mg/kg. The concentration is observed to be 27 times higher than the estimated European Cd average of topsoil which is 0.12 mg/kg (Aliu, Sajn, & Stafilov, 2009).

Alomary et al. (2012) has conducted a study in Irbid, Jordan and the result shows that the mean concentration of cadmium (3.31 mg/kg) is higher than those observed in Greece (0.2 mg/kg) and Turkey (2.53 mg/kg). However, it was found to be about 2 times lower than reported in central Jordan and South Jordan which were 4.98 mg/kg and 5.00 mg/kg respectively.

Besides, a study to detect the heavy metal dispersion was done by Dániel, Kovács, Prokisch, and Györi (2015) in Hungary. The data reveals that the total concentration of cadmium in soil was found to be ranged from 0.12 mg/kg to 2.82 mg/kg in topsoil. Also, a trend which the concentration decrease when moving right angle away from the road was reported in this study.

A mean concentration of 0.62 mg/kg with range of 0.10 mg/kg to 5.59 mg/kg was reported in a study done in Kowloon, Hong Kong. The value was close to the target value of 0.8 mg/kg. In addition to that, the mean value of cadmium in this study was also found to be compatible with two previous studies on urban soils in Hong Kong, having the mean

concentration of 2.18 mg/kg and 1.89 mg/kg respectively (Li, Lee, Wong, Shi, & Thornton, 2003).

2.4 Sources of Cadmium Contamination

In the study done by Chen et al. (2010), the result obtained shows that pollution from traffic was responsible for the higher mean concentration of cadmium in roadside soils in Beijing compared to the background values. This trend also shown in the study carried out in Irbid City, Jordan which the level of cadmium in area of high traffic density is higher compared to cadmium level along residential street. Several studies also show the relationship between traffic density and cadmium content which cadmium concentration decreased as the distance from the road increased (Bakirdere & Yaman 2008; Chen et al. 2010; Nabulo et al. 2006; Jankiewicz et al. 1999). For instance, a study done in Nigeria shows that the highest concentration of cadmium was detected at a high traffic density area with cadmium concentration of 28.64 µg/g (Akan et al. 2013). Also, factors such as domestic disposal or building construction also found to be contributed in the increase in cadmium concentration in soils (Massadeh, 2007). Cadmium contamination in soils also attributed to the use of cadmium in vehicles tires and fall-out from burning vehicle fuels as it would add to the soil through rainfall runoff from roads and pavements (Chen et al., 2010). Najib et al. (2012) reported that presence of cadmium in soil may be also due to the parent material in soil. Furthermore, highest cadmium content was found in the soils collected near the metal industry plant. The use of phosphate fertilizers in agriculture that contain a large amount of cadmium also causes a tendency to accumulate large amount of chemical element in soils (Deska et al., 1987).

2.5 Geoaccumulation Index

Geoaccumulation index was first proposed by Muller (1969) to assess the level of contamination of metals in sediments. However, it can also be used as a quantitative measure of metal contamination in soils (Loska, Wiechula & Korusa, 2004). Mathematically, geoaccumulation index is calculated by the following equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5 B_n}$$

where C_n is the concentration of the metal n , B_n is the background value of the metal and the factor 1.5 is the correction factor to account for lithogenic effect (Golekar, Baride, Patil & Yeole, 2013). Muller (1981) has classified the calculated geoaccumulation index into seven classes as presented in Table 1.

Table 1
Classification of I_{geo} (Muller, 1969)

Category	I_{geo}
Uncontaminated	$I_{geo} \leq 0$
Uncontaminated to moderately contaminated	$0 < I_{geo} \leq 1$
Moderately contaminated	$1 \leq I_{geo} \leq 2$
Moderately to heavily contaminated	$2 \leq I_{geo} \leq 3$
Heavily contaminated	$3 \leq I_{geo} \leq 4$
Heavily to extremely contaminated	$4 \leq I_{geo} \leq 5$
Extremely contaminated	$I_{geo} \geq 5$

Assessinents of heavy contamination in soils were done and geoaccumulation index was applied as qualitative measure in evaluating the anthropogenic influence and metal contamination in previous studies. The results from previous studies were presented in Table 2. As reported by Wei and Yang (2010), wide range of I_{geo} confirms variability of soil properties and sources of cadmium in these cities.

Table 2

Study areas and geoaccumulation index, I_{geo} of previous studies

Study Area	Geoaccumulation Index, I_{geo}	Reference
China	-0.46 to 3.60	Wei & Yang, 2010
Ghana	1.57 to 2.40	Agyarko, Darteh & Berlinger, 2010
Dexing, Jiangxi Province, China	0.89 to 4.30	Wei, Wang, Zhou & Qi, 2011
Bauchi, Nigeria	2.24 to 3.50	Butch.Chindo, Ekanem & Williams, 2013
Jalgaon District, Northern Maharashtra, India	-0.611 to 0.145	Golekar et al., 2013
Lakan, Iran	1.80 to 2.90	Ghadimi, Ghomi & Hajati, 2013

2.6 Effect of Soil pH

Soil pH is predominant factor in the sorption of heavy metal. The retention of cationic heavy metal tends to increase with the increase of soil pH. Study has been done and demonstrated that the metal sorption increase with the increase of soil pH. The result shows that a unit of increase in soil pH was followed by 36% increase in cadmium sorption (Appel & Ma, 2002). Ramakrishnaiah and Somashekar (2002) also proved that the mobility of cadmium is strongly dependent on soil pH. Besides, a study done by Naidu, Bolan, Kookana, and Tiller (1994) also showed the same trend where cadmium sorption increased with the increase of pH. According to Akan et al. (2003), increase in soil pH resulted in hydroxides and carbonates precipitation or formation of insoluble organic compounds, hence the mobility of heavy metal decreased. Above studies show that higher heavy metal concentration will be detected in soil as a consequence of alkaline nature of the soil.

2.7 Effect of Soil Organic Matter

Study done by Ramakrishnaiah and Somashekar (2002) showed a significant correlation between organic matter and cadmium concentration in soil. Due to the considerable effect of organic matter on CEC and the tendency of binding with organic

ligands to form stable complexes. organic matter became an important factor in heavy metal sorption. Adsorption of heavy metals in soil is affected by the amount of organic matter (Karaca, 2006). Some studies showed that alteration of contaminated soils with organic matter reduced bioavailability of heavy metals (Kham et al. 2000). As reported by Babejova, Dlapa, and Pis (2001), an increase in total organic carbon content caused an increase in cadmium adsorption in soil.

3.0 Materials and Methods

3.1 Study Area and Sampling Locations

Kuching City, state capital of Sarawak, Malaysia was chosen to be the study area. It has the highest population in Sarawak which is 329,200 (Official Website of Kuching District Office, 2014). Rapid urbanization and industrialization in this urban city has brought a lot of impacts on the environment.

Samajaya Free Industrial Zone and BDC was selected to be the soil sampling sites. Samajaya is an industrial area which traffic density is high during rush hours and may exert some anthropogenic pressure from industrial wastes. BDC is housing area which is less affected yet still exerts some pressures from municipal waste and automobile emission.

3.2 Sample Collection

The top soil between the depth of 0 to 20 cm was collected using a stainless steel trowel. The soil samples were then placed in plastic bags with labels and transported to laboratory (Najib et al. 2012). 10 soil samples were collected randomly from each sampling sites. Each of the samples was a composite sample. A total of 20 soil samples were collected on 1st December 2014. The samples were collected inside labeled polyethylene bags and transported to laboratory for pre-treatment. Locations of the sampling sites were identified using a GPS. Table 3, Figure 1 and Figure 2 show the sampling points where soils samples were collected. Besides, reference soil sample from a protected area (forest) located far from anthropogenic influences was obtained for the purpose of contamination assessment.

Table 3

Coordinates of all the sampling points

Sampling Site	Sampling Point	Coordinate	Description
Samajaya	1	N 01°30'43.4" E 110°23'06.2"	It is located at a main roundabout in front of Samjaya Free Industrial Zone entrance and near the construction area. Dense traffic was observed during pick hours.
	2	N 01°30'47.5" E 110°23'25.5"	It is located at a main roundabout.
	3	N 01°31'07.3" E 110°24'00.3"	It is located at the construction area, near the factory and cleared land.
	4	N 01°31'22.1" E 110°24'20.9"	It is located near the X-FAB factory.
	5	N 01°31'06.3" E 110°24'36.9"	It is located near the dumping site, river and X-FAB Factory.
	6	N 01°31'39.7" E 110°24'21.4"	It is located near the factory and Datuk Kawada Indoor Stadium.
	7	N 01°31'28.3" E 110°23'43.3"	It is located near the Lintec Industries and in front of residential area. A lot of rubbish was found there.
	8	N 01°31'27.7" E 110°23'30.3"	It is located at a playground opposite a new residential area and cleared land.
	9	N 01°31'26.7" E 110°23'07.3"	It is located at a playground and near Taman Rimba Samajaya Forest.
	10	N 01°31'44.6" E 110°23'15.2"	It is located in front of shophot near a construction area. Dense traffic was observed.
BDC	1	N 01°30'16.6" E 110°21'06.2"	It is located at a playground in the residential area. Rubbish and a lot of dry leaves were found there.
	2	N 01°29'54.7" E 110°21'00.0"	It is located at the roadside. A lot of rubbish was found and open burning was observed.
	3	N 01°30'12.9" E 110°20'56.5"	It is located in front of shophot of the residential area near a small construction site.
	4	N 01°30'14.6" E 110°20'43.2"	It is located at a main roundabout.
	5	N 01°30'23.4" E 110°20'52.4"	It is located within the housing area and a lot of dry leaves were found.
	6	N 01°30'19.4" E 110°21'07.3"	It is located near the main road.
	7	N 01°30'26.2" E 110°21'05.1"	Crops were planted there.
	8	N 01°30'35.3" E 110°21'14.5"	Plastic garbage and a lot of trees were found there.
	9	N 01°30'33.9" E 110°21'22.3"	It is located near the shophot, swimming pool and mosque.
	10	N 01°30'25.9" E 110°21'22.6"	It is located opposite to a cleared land.



Figure 1: Sampling points at Samajaya Free Industrial Zone.



Figure 2: Sampling points at BDC.

3.3 Soil Preparation

The contaminants in soil samples such as stone, leaves or twigs were removed and dried in room temperature. The samples were ground using mortar and sieve using 2.00 mm and 0.425 mm sieve to obtained homogenized powder (Chen et al., 2010).

3.4 Soil Analysis

3.4.1 Determination of Soil pH

5g of 2.00 mm of soil was put in a centrifuge tube. 25 mL of distilled water was added to the sample to make a 1:5 soil solution. The centrifuge tube was placed on the shaker to shake at 120 rpm for 1 hour. After shaking, the pH of the solution was measured using pH meter.

3.4.2 Determination of Soil Organic Matter (SOM)

Initial weight of crucible was taken by placing the crucible in oven overnight at 105°C. This procedure was repeated to obtain the constant weight. 3 g of soil sample (0.425 mm) was placed into the crucible. The weight of the crucible with sample was recorded. It was then placed in oven at 105°C for 24 hours and the weight was recorded. After that, the crucible was placed in the furnace at the temperature of 550 °C for 8 hours. The weight was then recorded after the crucible was cooled down in a desiccator. Following is the formula used to calculate the soil organic matter.

$$SOM = \frac{O_{dw} - R_w}{O_{dw}} \times 100$$

O_{dw} : Weight of oven-dried sample

R_w : Residual weight ^Weight of ashed sample